PATENT SPECIFICATION

NO DRAWINGS

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858,079

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COMPLETE SPECIFICATION

Improvements in or relating to the Combination of Hydrogen and Oxygen

SPECIFICATION NO. 858,079

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of Engelhard Industries, Inc., a corporation organised and existing under the laws of the State of Delaware, United States of America, of 113, Astor Street, Newark 2, New Jersey, United States of America.

THE PATENT OFFICE,
March 1, 1961

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gen and oxygen derived from the decomposition of water in nuclear reactors.

The presence of uncombined hydrogen and oxygen in streams derived from nuclear reactors is troublesome for a number of reasons, one of which is that the gas pressure increases unless the system is vented and, where the vapor contains radioactive materials, such venting is a hazardous procedure. Another difficulty is that explosions may occur if the hydrogen and oxygen concentrations become appreciable and even in situations where these concentrations are low, the explosion hazard must always be considered. For example, if steam is condensed, such as the steam from a turbine, the hydrogen-oxygen concentration will be multiplied many times, converting an innocuous stream into one which is potentially hazardous. A third difficulty resides in the corrosive effects of hydrogen and oxygen on materials of construction at elevated temperatures. For these reasons, it is desirable, and sometimes mandatory, that the hydrogen and oxygen be recombined to water, and reactors are often equipped containing water vapor or steam. These catalysts retain their initial high activity, and the strength thereof is unaffected by exposure to steam. The term "platinum group metal" is used as meaning platinum, palladium, iridium, rhodium, osmium or ruthenium.

The catalyst support employed is silica-alumina having a surface area in excess of 30 square metres per gram, and the silica content is, at least, 4 per cent by weight of the carrier. The catalytic metal may be present in the range of from 0.1 to 5 per cent by weight of the combined catalytic metal and support, and of the various platinum group metals, palladium is preferred. If desired, a mixture of platium group metals, e.g. platinum and rhodium, may be employed. The supported catalyst may be prepared in any suitable manner, i.e. by treating the carrier or support with a solution of a suitable metal compound and then reducing the metal compound to metal.

The temperature in the catalytic unit containing the catalyst may be in the range of

[*Price 3s. 6d.*]

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Improvements in or relating to the Combination of Hydrogen and Oxygen

We, ENGELHARD HANOVIA, INC., formerly ENGELHARD INDUSTRIES, INC., a Corporation duly organised under the laws of the State of New Jersey, United States of America, of 100, Chestnut Street, Newark 5, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to an improved catalytic process for combining hydrogen and oxygen in the presence of steam or water vapor and, more particularly, the invention relates to the chemical combination of hydrogen and oxygen derived from the decomposition of water in nuclear reactors.

The presence of uncombined hydrogen and oxygen in streams derived from nuclear reactors is troublesome for a number of reasons, one of which is that the gas pressure increases unless the system is vented and, where the vapor contains radioactive materials, such venting is a hazardous procedure. Another difficulty is that explosions may occur if the hydrogen and oxygen concentrations become appreciable and even in situations where these concentrations are low, the explosion hazard must always be considered. For example, if steam is condensed, such as the steam from a turbine, the hydrogen-oxygen concentration will be multiplied many times, converting an innocuous stream into one which is potentially hazardous. A third difficulty resides in the corrosive effects of hydrogen and oxygen on materials of construction at elevated temperatures. For these reasons, it is desirable, and sometimes mandatory, that the hydrogen and oxygen be recombined to water, and reactors are often equipped with recombining equipment, much of which is catalytic.

Processes for the catalytic combination of hydrogen and oxygen in essentially dry gases are well known, and the preferred catalyst is usually palladium or platinum on alumina having a high surface area. However, when these catalysts are used in contact with gas streams of high water vapor content, and at elevated temperatures, they lose activity and the strength thereof deteriorates.

In accordance with the present invention, it has been found that nickel, or a platinum group metal, either singly or in combination, supported on a silica-alumina carrier, is a particularly advantageous catalyst for recombining hydrogen and oxygen in gas streams containing water vapor or steam. These catalysts retain their initial high activity, and the strength thereof is unaffected by exposure to steam. The term "platinum group metal" is used as meaning platinum, palladium, iridium, rhodium, osmium or ruthenium.

The catalyst support employed is silica-alumina having a surface area in excess of 30 square metres per gram, and the silica content is, at least, 4 per cent by weight of the carrier. The catalytic metal may be present in the range of from 0.1 to 5 per cent by weight of the combined catalytic metal and support, and of the various platinum group metals, palladium is preferred. If desired, a mixture of platium group metals, e.g. platinum and rhodium, may be employed. The supported catalyst may be prepared in any suitable manner, i.e. by treating the carrier or support with a solution of a suitable metal compound and then reducing the metal compound to metal.

The temperature in the catalytic unit containing the catalyst may be in the range of

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maintained above the dew point of the mixture.

2. A process according to Claim 1 in which the catalytic metal is palladium.

3. A process according to Claim 1 in which the catalytic metal is a mixture of platinum and rhodium.

4. A process according to Claim 1 in which the catalytic metal constitutes from 0.1 to 5 per cent of the combined weight of the catalytic metal and support.

5. A process according to Claim 1 in which the catalytic metal is maintained at a temperature in the range of from 100 to 800° C.

6. A catalytic process for combining hydrogen and oxygen in the presence of steam, substantially as described in Example II of the foregoing examples.

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from 100 to 800° C., with the additional proviso that the catalyst temperature must be maintained above the dew point. The preferred temperature range is about 100 to 500° C.

The reaction pressure may be in the range of subatmospheric to super-critical, i.e., greater than 3200 psig. There are no limitations upon the reaction pressure as long as the dew point limitation is observed.

The space velocity of the gases passed over the catalyst may be in the range of from 10 to 50,000 standard volumes of vapor per volume of catalyst per hour, preferably 5,000 to 20,000 standard volumes per volume per hour.

The gas compositions which may be treated in accordance with the present invention are steam, either saturated or superheated, containing hydrogen and oxygen in stoichiometric proportions. Gas compositions containing high percentages of water vapor, in addition to hydrogen and oxygen, may also be treated in accordance with the present invention. Aside from catalyst considerations, safe practice will limit the hydrogen and oxygen concentrations to values below the explosive limit. In mixtures where the two gases are not present in stoichiometric proportions, the catalytic treatment will remove the minor constituent quantitatively, leaving the unreacted excess of the other constituent in the stream.

The invention will be further illustrated by reference to the following specific examples:—

Example I

A catalyst was prepared as follows:—

Commercial $\frac{1}{8}$" diameter silica-alumina spheres were used as the catalyst carrier. Specifications of this carrier are 85% Al_2O_3, 2.0% Na_2O, 0.15% Fe, 6.3% SiO_2, and 6.2% loss on ignition.

The spheres were treated with Na_2PdCl_4 and Na formate solution and heated, with the formation of a black Pd deposit on the outside of the spheres, after which they were washed.

The catalyst was then dried in an oven at a temperature of 100° C., and assayed as follows:—

Palladium - -	0.40 per cent
Water solubles -	0.054 per cent
Chlorine - - -	trace

Example II

A stainless steel apparatus was used to expose the catalyst prepared in Example I above, to high-pressure steam, under conditions closely simulating those used in one type of nuclear reactor application. Since the reactor itself effected some oxygen removal, the catalyst was evaluated for activity in a separate reactor, fabricated from high silica glass. The evaluation was made at the same temperature as the exposure, i.e. 450° C., but at atmospheric pressure rather than the pressure of 600 psig. used in the steam exposure test.

A 100 ml. charge of the catalyst prepared in Example I above, was placed in the stainless steel reactor, and steam from a high-pressure boiler was passed through the catalyst bed at a pressure of 600 psig. The reactor was electrically heated to superheat the steam to a temperature of 450° C.; the vapor flow rate was 400 grams per hour. After 37 hours of exposure under these conditions, the catalyst was removed from the stainless steel reactor, and 50 ml. thereof were charged to a high silica glass reactor, the latter reactor being connected to the same boiler, which contained electrodes for the electrolytic decomposition of a sodium hydroxide solution contained therein. Current was passed through the combination boiler-electrolyzer such that 400 grams per hour of steam, containing 228 volumes per million volumes of oxygen and the stoichiometric equivalent of hydrogen, passed through the high silica glass reactor at atmospheric pressure and at a temperature of 450° C. The effluent from the reactor was condensed at room temperature, and the residual gas was swept, by means of deoxygenated hydrogen, into a sensitive analyzer (Hersch meter) for oxygen determination.

The oxygen in the effluent stream was calculated to be less than 0.5 part per million, this being the limit of detection. The average crushing strength of the spheres was 10 pounds, which was essentially the same, within experimental error, as for unexposed spheres. In another empirical test of strength, loss by attrition was about 1 per cent by weight in six hours, which is also essentially unchanged from the attrition rate of fresh catalyst.

In contrast to these results, the following results were found using a catalyst consisting of 0.5 per cent by weight palladium on essentially pure alumina, tested under identical conditions with those given above. Oxygen in the effluent gas was greater than 20 parts per million, when 228 parts per million were present in the inlet gas, and 2 parts per million in the effluent when 9 parts per million were present in the inlet gas. The crushing strength was 1.6 pounds versus 5.3 pounds for the fresh catalyst, and the attrition loss was 28 per cent by weight in 4 hours for the exposed catalyst, versus 5 per cent by weight for the fresh catalyst.

WHAT WE CLAIM IS:—

1. A process for combining hydrogen and oxygen in the presence of steam which comprises contacting the mixture with a catalytic metal selected from the group consisting of nickel and a platinum group metal supported on a silica-alumina carrier having a surface area in excess of 30 square metres per gram and a silica content of at least 4 per cent by weight, the catalytic metal temperature being